

(19)



JAPANESE PATENT OFFICE

PATENT ABSTRACTS OF JAPAN

(11) Publication number: **05110138 A**

(43) Date of publication of application: **30.04.93**

(51) Int. Cl

H01L 33/00

H01L 21/205

(21) Application number: **03292303**

(71) Applicant: **NICHIA CHEM IND LTD**

(22) Date of filing: **12.10.91**

(72) Inventor: **NAKAMURA SHUJI**

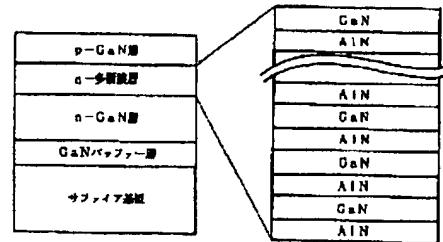
**(54) GROWING METHOD FOR CRYSTAL OF
GALLIUM NITRIDE COMPOUND
SEMICONDUCTOR AND ELEMENT THEREOF**

(57) Abstract:

PURPOSE: To obtain a crystal of p-n junction gallium nitride compound semiconductor excellent in crystallizability.

CONSTITUTION: When a buffer layer represented by general formula $GaXAl_{1-X}N$ ($0 \leq X \leq 1$) and multilayer film layer, which is obtained when thin-film AlN layers and GaN layers are alternately grown in at least one layer laminated on the buffer layer, are grown on a substrate; the lattice defect of GaN is stopped by the multilayer film layer.

COPYRIGHT: (C)1993,JPO&Japio



[Claim(s)]

[Claim 1] It is the crystal growth approach which carries out the laminating of the crystal of the gallium nitride system compound semiconductor by which a general formula is expressed with $\text{GaXAl}_1\text{-XN}$ ($0 \leq X \leq 1$) on a substrate. (a) The process into which the buffer layer as which a general formula is expressed in $\text{GaXAl}_1\text{-XN}$ ($0 \leq X \leq 1$) on a substrate is grown up, (b) The crystal growth approach of the gallium nitride system compound semiconductor characterized by including the process into which the multilayers layer into which the AlN layer and GaN layer of a thin film were grown up by turns is grown up.

[Claim 2] The component which the gallium nitride system compound semiconductor by which a general formula is expressed with $\text{GaXAl}_1\text{-XN}$ ($0 \leq X \leq 1$) on a substrate is the component by which the laminating was carried out, and is characterized by having the multilayers layer the AlN layer and GaN layer of a thin film grew up to be by turns in the buffer layer as which a general formula is expressed in $\text{GaXAl}_1\text{-XN}$ ($0 \leq X \leq 1$) on said substrate, and at least one layer by which the laminating was carried out on it.

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the component obtained by the crystal growth approach which can raise the crystallinity of a gallium nitride system compound semiconductor especially, and its approach about the crystal growth approach of a gallium nitride system compound semiconductor and component which can be used for blue light emitting diode and blue luminescence laser diode etc.

[0002]

[Description of the Prior Art] Research is advanced using an II-VI group's ZnSe, an IV-IV group's SiC, an III-V group's GaN, etc., it is announced that luminescence in which the gallium nitride system compound semiconductor [$\text{GaXAl}_1\text{-XN}$ ($0 \leq X \leq 1$)] was comparatively excellent also in it with ordinary temperature is shown recently, and the blue luminescence device attracts attention.

[0003] As an approach of growing up the crystal of a gallium nitride system compound semiconductor, vapor growth, such as organometallic compound vapor growth (henceforth the MOCVD method) and a molecular beam epitaxy method (henceforth the MBE method), is known well. When the approach using the MOCVD method is explained briefly, for example, this approach Supply organometallic compound gas (trimethylgallium, trimethylaluminum, ammonia, etc.) as reactant gas in the reaction container which installed silicon on sapphire, and crystal growth temperature is held to an about 900 degrees C - 1100 degrees C elevated temperature. They are n mold and p mold (p mold is not yet realized.) about a gallium nitride system compound semiconductor, growing up the epitaxial layer of a gallium nitride system compound semiconductor, and supplying other reactant gas if needed on a substrate. It is the approach of carrying out a laminating.

[0004]

[Problem(s) to be Solved by the Invention] MOCVD -- law and MBE -- the thing most important when carrying out vapor growth of the gallium nitride system compound semiconductor like law is whether to carry out the laminating of the crystal of the compound semiconductor which has the crystallinity which was [how] excellent.

[0005] for example, if epitaxial growth is directly performed on silicon on sapphire at an elevated temperature in GaN, since the surface state of a crystal layer and crystallinity will get remarkably bad, before performing epitaxial growth at an elevated temperature, it is shown clearly by forming the buffer layer which consists of AlN and performing epitaxial growth at an elevated temperature on a buffer layer continuously by the low temperature around 600 degrees C first that the crystallinity of GaN is markedly alike and improves (JP,2-229476,A). Moreover, this invention person showed that the laminating of the crystalline gallium nitride system compound semiconductor excellent in the direction which makes GaN a buffer layer rather than the conventional approach of making AlN a buffer layer could be previously carried out in Japanese Patent Application No. No. 89840 [three to].

[0006] Thus, although the crystallinity of a gallium nitride system compound

semiconductor is very good by forming a buffer layer, it is still inadequate for putting in practical use the luminescence device of which the crystallinity which was extremely excellent like the blue light emitting diode of high power and blue laser, for example is required. That is because the p-n junction of the layers excellent in crystallinity is unrealizable.

[0007] This invention is accomplished in view of such a situation, and since high power blue light emitting diode, blue luminescence laser, etc. are put in practical use, the place made into the purpose offers the component obtained by the growth approach to which the crystal of the gallium nitride system compound semiconductor excellent in crystallinity can be obtained, and its approach.

[0008]

[Means for Solving the Problem] The crystal growth approach of this invention is the crystal growth approach which carries out the laminating of the crystal of the gallium nitride system compound semiconductor by which a general formula is expressed with $\text{GaXAl}_1\text{-XN}$ ($0 \leq X \leq 1$) on a substrate. It is characterized by including the process into which the multilayers layer into which the process into which the buffer layer as which a general formula is first expressed in $\text{GaXAl}_1\text{-XN}$ ($0 \leq X \leq 1$) on a substrate is grown up, and the AlN layer of a thin film and the GaN layer of a thin film were grown up by turns is grown up. Although there are sapphire, SiC, Si, etc. in a substrate, generally sapphire is used.

[0009] The crystal growth approach of this invention is explained about the case where the crystal of GaN is grown up into C side of silicon on sapphire for example, using the MOCVD method. First, the silicon on sapphire washed beforehand is installed in the susceptor in a reaction container, among reducing atmosphere, a susceptor is heated at 1000 degrees C or more by high-frequency heating etc., and the oxide on a substrate is removed. After cooling slowly and lowering the temperature of a susceptor even before and after 600 degrees C after heating, reactant gas is supplied in a reaction container and the buffer layer of $\text{GaXAl}_1\text{-XN}$ ($0 \leq X \leq 1$) is first grown up on a substrate. Reactant gas

uses ammonia gas as organometallic compound gas, such as trimethylaluminum (TMA), and a source of N as trimethylgallium (TMG) and a source of aluminum as a source of Ga. After growing up a buffer layer, temperature of a susceptor is made into an elevated temperature 900 degrees C or more, it holds at 1050 degrees C, and TMG gas and ammonia gas grow up the crystal of GaN with a sink. In obtaining the GaN layer of n mold, it usually dopes Si for silane gas during a sink GaN crystal with those gas. Here, when putting in the multilayers layer of this invention into n type layer, TMG gas and TMA gas can be formed in the middle of growth of the n mold GaN layer by turns by carrying out the laminating of the thin film of GaN and AlN with a sink. In addition, although it is not necessary to pass especially silane gas in the middle of growth of this multilayers layer, crystalline high n type layer is obtained more for the passed direction. A sink n mold GaN layer is again formed for TMG gas, TMA gas, and silane gas after the multilayers stratification. Next, in forming a p mold GaN layer on an n mold GaN layer, in addition to TMG gas and TMA gas, diethyl zinc (DEZ), magnesium cyclopentadienyl (Cp_2Mg) gas, etc. are passed, and it dopes Zn or Mg in a GaN layer. In addition, a multilayers layer may be put in during growth of this p type layer.

[0010] In the crystal growth approach of this invention, the buffer layer first grown up on a substrate is surely required, in order to raise the crystallinity of the gallium nitride system compound semiconductor to be grown up from now on. Although the general formula can be expressed with $GaXAl_{1-X}N$ ($0 \leq X \leq 1$), $GaAlN$ is made into a buffer layer and the buffer layer of GaN is [crystallinity is / direction / desirable and] the most desirable rather than it makes AlN into a buffer layer, as this invention person clarified before. The growth temperature of a buffer layer is usually 200 degrees C - 900 degrees C low temperature. for example, MOCVD -- although it is around 600 degrees C in law -- MBE -- it can be made to grow up at the temperature not more than it by law

[0011] A multilayers layer carries out the laminating of the GaN crystal film and the AlN crystal film, respectively. With any ingredients other than this, it cannot grow up with sufficient crystallinity. Growth temperature can be formed at the same temperature as the

temperature at the time of growing up a gallium nitride system compound semiconductor crystal. Moreover, the laminating of a GaN layer and the AlN layer is carried out more than two-layer by 10-3000A thickness, respectively, and they usually carry out a 10-100-layer laminating by the thickness around 20-500A. When it is difficult to stop the lattice defect described later if the total thickness of multilayers is thinner than 20A and each thickness is larger than 3000A, it is in the inclination for the crystallinity of the multilayers layer to worsen. Even if the thickness of each layer is the same, it may differ. Furthermore, if a multilayers layer is the middle of growing up the crystal of a gallium nitride system compound semiconductor as mentioned above, it may be formed into which layer, for example, can be formed in the middle class of p type layer on n type layer in n type layer on a buffer layer.

[0012]

[Function] An operation of the multilayers layer of this invention is explained. As for silicon on sapphire (C side) and GaN, the lattice constant has shifted about 16%. The gap is still larger if it results in AlN. A big distortion occurs between silicon on sapphire and a GaN layer by the difference in this lattice constant. Furthermore, a lattice defect is made by this distortion into a GaN layer, and this defect runs continuously to the last during GaN growth. For this reason, the multilayers layer of this invention has the operation which can be stopped here by carrying out the laminating of the thin film material which is different on the way in this defect made continuously.

[0013] Moreover, the sectional view of the component obtained by drawing 1 according to one example of the crystal growth approach of this invention is shown. This drawing is what carried out the laminating of n mold multilayers layer which carried out the laminating of the thin film of AlN and GaN, and the p mold GaN layer which doped Mg to order, doping a GaN layer, the n mold GaN layer which doped Si, and Si on silicon on sapphire, can stop said lattice defect in an n mold GaN layer by this multilayers layer, and since the p mold GaN layer excellent in crystallinity is obtained, it can realize p-n junction of the outstanding property.

[0014]

[Example] The crystal growth approach of this invention is explained in full detail in the example below.

[Example 1]

** Install the silicon on sapphire washed well first in the susceptor in a reaction container. After carrying out evacuation of the inside of a container, the substrate was heated for hydrogen gas for 20 minutes at 1050 degrees C with the sink, and the surface oxide was removed. Then, temperature was cooled even at 500 degrees C, it considered as the source of Ga in 500 degrees C, and the GaN buffer layer was grown up by 200A thickness with the sink in hydrogen gas as ammonia gas and carrier gas as TMG gas and a source of N.

[0015] ** After raising only TMG gas next and raising a stop and temperature even at 1030 degrees C, the sink and the Si dope n mold GaN layer were again grown up by 4-micrometer thickness in TMG gas and SiH4 (mono silane) gas.

[0016] ** next, TMA gas after TMA gas grew up [TMG gas] 100A of sink AlN layers as a stop and a source of aluminum -- a stop -- similarly TMG gas grew up 100A of sink GaN layers again. This actuation was repeated 15 times by turns, and the multilayers layer of Si dope which consists of 15 layers of AlN layers and 15 layers of GaN layers was grown up.

[0017] ** Cp2Mg gas newly grew up the Mg dope p mold GaN layer by the thickness of 0.5 micrometers on the multilayers layer succeedingly with the sink, and the stop and the component which has the crystal of the gallium nitride system compound semiconductor of this invention were obtained for SiH4 gas and AlN gas.

[0018] The component which a multilayers layer is not grown up in [example 1 of comparison] **, and also has the crystal of a gallium nitride system compound semiconductor like an example 1 was obtained.

[0019] Thus, the following trials were performed in order to evaluate the crystallinity of a gallium nitride system compound semiconductor crystal of the component of the example 1 and the example 1 of a comparison which were acquired.

[0020] First, helium-Cd laser is irradiated at p type layer, photoluminescence measurement

is performed, and the result is shown in drawing 2 R> 2. As shown in this drawing, blue luminescence reinforcement [in / in the direction of the component obtained in the example 1 / those 450nm] is clearly large, and it turns out that the crystallinity of GaN of p type layer is excellent.

[0021] Next, the double crystal X-ray rocking curve of p type layer was measured, and it was asked for the half-value width (FWHM:full width at half-maximum). It can be considered that the crystallinity is excellent, so that FWHM is small. Consequently, it of the example of a comparison was 5 minutes to the component of an example 1 having been 3 minutes.

[0022] Furthermore, after making the obtained component the chip of 0.5mm angle by dicing, blue light emitting diode (LED) was produced and was made to emit light by taking out an electrode from p type layer and n type layer, setting to a leadframe according to a conventional method, and giving resin mold. Consequently, in 20mA of forward current, it passed over it of the example 1 of a comparison only to 35microA to the radiant power output of LED obtained from the component of an example 1 having been 70 microwatts. Moreover, it of the example of a comparison was 20V to the forward voltage of LED of an example 1 having been 4V.

[0023] In the process of [example 2] **, the component which the laminating of an AlN layer and every 20 layers of the GaN layers is carried out by 200A thickness, respectively, and also has the crystal of the gallium nitride system compound semiconductor of this invention like an example 1 was obtained.

[0024] When this component as well as photoluminescence measurement, FWHM measurement, and blue light emitting diode performed crystalline evaluation, the almost same result as the component obtained in the example 1 was obtained.

[0025] In the process of [example 3] **, the component which the laminating of an AlN layer and every ten layers of the GaN layers is carried out by 50A thickness, respectively, and also has the crystal of the gallium nitride system compound semiconductor of this invention like an example 1 was obtained.

[0026] When this component as well as photoluminescence measurement, FWHM

measurement, and blue light emitting diode performed crystalline evaluation, the almost same result as the component obtained in the example 1 was obtained.

[0027] TMG gas raised a stop and temperature to 1030 degrees C after the process of [example 4] **, succeedingly, similarly, the process of ** was performed and the component which a multilayers layer is formed like ** on a buffer layer, and also has the crystal of the gallium nitride system compound semiconductor of this invention like an example 1 was obtained. (Order of **-**-**-**)

[0028] When this component as well as photoluminescence measurement, FWHM measurement, and blue light emitting diode performed crystalline evaluation, the almost same result as the component obtained in the example 1 was obtained.

[0029] In [example 5] **, the component which replace with a GaN buffer layer, and an AlN buffer layer is grown up to be a buffer layer by 200A thickness, and also has the crystal of the gallium nitride system compound semiconductor of this invention like an example 1 was obtained.

[0030] When this component performed crystalline evaluation similarly, as for 10% fall and FWHM, some was worse than what was obtained in 63 microwatts of radiant power outputs of blue light emitting diode, and forward voltage 6V and an example 1 for 3.8 minutes from that from which photoluminescence reinforcement was obtained in the example 1.

[0031]

[Effect of the Invention] the manufacture approach of this invention prepares first the crystallinity of the gallium nitride system compound semiconductor which grows on it by the buffer layer, and since it can stop the lattice defect of the crystal further generated by gap of a lattice constant in a multilayers layer, the crystallinity of a crystal which carried out the laminating can be boiled markedly, and it can raise it.

[0032] as explained above, according to the manufacture approach of this invention, the crystallinity of a gallium nitride system compound semiconductor layer is markedly alike, and improves. Therefore, as for the component obtained by the approach of this invention,

a great thing has a merit on industry towards utilization of blue luminescence devices, such as a blue light emitting diode which was not able to be put in practical use until now, and blue luminescence laser, etc.

[Brief Description of the Drawings]

[Drawing 1] The mimetic diagram showing the cross section of the component by one example of the crystal growth approach of this invention.

[Drawing 2] Drawing measuring and showing the luminescence reinforcement by photoluminescence measurement with the component by one example of the crystal growth approach of this invention, and the component by the conventional method.